Electrical Resistance and Crack Behaviors of Carbon Nanotube-based Polymer Composites

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論文内容要旨

Chapter 1　　Introduction

In general, nanotechnology can be understood as a technology of design, fabrication, and applications of nanostructures and nanomaterials. Nanotechnology also includes fundamental understanding of properties and phenomena of nanostructures and nanomaterials. Recent advances in producing nanomaterials with novel properties have stimulated research to create macroscopic engineering materials that can exploit these properties. Motivated by the recent enthusiasm in nanotechnology, development of nanocomposites is one of the rapidly evolving areas of composites research.

Carbon nanotubes (CNTs) are the most intensively studied nanomaterials for composite production. Carbon nanotubes occur in two general forms: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs can generally be visualized as a rolled up sheet of graphene which is a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice. They have diameters as small as 0.4 nm and normally no larger than 2 nm. MWNTs can be viewed as several concentric SWNTs with outside diameters that range between 5 nm and 100 nm. The interlayer spacing of MWNTs is approximately 0.34 nm, and this value is also widely taken as the thickness of individual CNT layers. It is also known that both SWNTs and MWNTs have a high aspect ratio (length/diameter) in the range of 100-10,000. The densities of SWNTs and MWNTs are reported to be about 0.8 and 1.8 g/cm^3, respectively. Nanotube properties are influenced by atomic arrangement (chirality), nanotube diameter and length, and morphology (straight, waved, coiled, etc.).

To date, a number of researchers have employed both theoretical and experimental techniques to determine the physical and mechanical properties of CNTs. Due to the extremely small size of CNTs, the experimental studies are challenging, and the results normally show significant variability. This could also be attributed to differences in the CNT structure, existing defects, and synthesis techniques. In theoretical studies, researchers have used modeling methods accounting for all length scales to characterize the behavior of CNTs. The theoretical predictions tend to overestimate the physical and mechanical properties when compared with experimental findings, which assume that the CNT is a defect-free structure. Theoretical and experimental results have shown the elastic modulus and strength of CNTs ranging about 0.3-1 TPa and 10-500 GPa, respectively. CNTs have the high elastic modulus and strength as a result of the carbon-carbon sp^2 bonding. In contrast to planar graphene, the cylindrical shape provides nanotubes with structural stability under compression. The electrical properties of CNTs have also attracted a great deal of interest from the research community. Their nanoscale dimensions, coupled with the unique electronic structure of the host graphene sheet, lead to a variety of unique electrical properties. These properties have been extensively investigated both theoretically and experimentally. Several groups have reported electrical conductivity results for SWNTs and MWNTs, and the electrical conductivity of individual CNTs is essentially in the order of 10^4-10^7 S/m.

The unique physical and mechanical properties of nanotubes combined with their high aspect ratio and low density have brought about extensive research in creating composite material systems to exploit these properties. The progress made in the production and purification of CNTs has made it practical to use CNTs as nanoscale fillers in polymeric materials. Considerable interest has focused on incorporating nanotubes into polymeric materials in order to tailor physical and mechanical properties such as stiffness, strength and electrical conductivities. Such CNT-based polymer composites may offer numerous engineering applications including aircraft and spacecraft, automobiles and cryogenic systems. There are two main types of polymers used for composites: thermosets (epoxy, polyimide, etc.) and thermoplastics (poly methyl methacrylate (PMMA), poly ether ether ketone (PEEK), polycarbonate, etc.). Thermoplastics have several advantages over thermosets, including reformability, recyclability, low cost, and superior damage tolerance and strength. These advantages, especially excellent mechanical properties, make them well-suited for cryogenic composites. Thus CNT-based thermoplastic polymer composites can be thought to be a promising candidate for cryogenic applications, and we investigated some basic performance of the nanocomposites at cryogenic temperatures.

CNT-based polymer composites are multifunctional materials that, in addition to their basic functions of physical and mechanical properties enhancement, allow the sensing and monitoring of strain or damage by the measurement of the material electrical resistance. The principle behind this is that the deformation of CNT-based polymer composites or the damage initiation and evolution in the nanocomposites can lead to changes in their electrical resistance. These electrical resistance changes provide the possibility of real-time health monitoring, which improves the safety of structures. In order to fully explore the potential of CNT-based polymer composites for engineering applications, an in-depth understanding of their performance is necessary.

There have been numerous studies on the electrical response of CNT-based polymer composites. It has been theoretically and experimentally confirmed that the electrical conductivity of CNT-based composites depends on many factors such as nanotube type (SWNT and MWNT), nanotube length, nanotube waviness, contact resistance between nanotubes, etc. Also, several studies on strain/damage sensing utilizing the electrical resistance of CNT-based polymer composites have appeared in the literature, and their sensing capabilities were demonstrated. However, relatively little analytical work has been conducted. Although numerical methods have the best potential for accurately predicting composite behaviors, such approaches lead to time demanding computations and often it is difficult to gain physical insights into the phenomena occurring in the composites. In contrast, analytical solutions provide quick methods of analyzing a problem and give a clear physical interpretation of the results. Such an analytical model may also yield knowledge of how the nanoscale phenomena influence the bulk properties and useful information for design of the nanostructure to create multifunctional composites. Therefore, an analytical model to predict the electrical resistance behavior of CNT-based polymer composites is necessary.

It was reported that CNT-based composites inherently contain some sort of imperfections in the form of either small voids or cracks. When subjected to mechanical stresses in service, these composites can fail prematurely due to the propagation of these flaws. Therefore, a systematic study on the crack behavior in CNT-based composites is necessary so that they can be used with confidence. Due to their wide potential applications, it is important to know the crack behavior of CNT-based polymer composites under various operating conditions (temperature, loading mode, loading rate, etc.).

This paper presents a systematic theoretical and experimental study on the electrical resistance and crack behaviors of CNT-based polymer composites. The outlines of each chapter are described below.

Chapter 2 Modeling and Characterization of the Electrical Conductivity of Carbon Nanotube-based Polymer Composites

In this chapter, we investigate both analytically and experimentally the electrical properties of CNT-based polymer composites. An analytical model was developed to predict the electrical conductivity of CNT-based composites. The micro/nanoscale structures of the nanocomposites and the electrical tunneling effect due to the matrix material between CNTs were incorporated within the model. Electrical conductivity measurements were also performed on CNT/polycarbonate composites to identify the dependence of their electrical transport characteristics on the nanotube content. The analytical predictions were compared with the experimental data, and a good correlation was obtained between the predicted and measured results. In addition, the effect of nanotube geometry on the nanocomposite electrical properties at the macroscale was examined.

Chapter 3 Electrical Resistance-based Strain Sensing in Carbon Nanotube/Polymer Composites under Tension: Analytical Modeling and Experiments

This chapter presents an analytical and experimental study on the strain sensing behavior of CNT-based polymer composites. Tensile tests were conducted on CNT/polycarbonate composites and the responses in the electrical resistance were measured during the tests. An analytical model incorporating the electrical tunneling effect due to the matrix material between CNTs was also developed to describe the electrical resistance change as a result of mechanical deformation. The model deals with the inter-nanotube matrix deformation at the micro/nanoscale due to the macroscale deformation of the nanocomposites. A comparison of the analytical predictions and the experimental data showed that the proposed model captures the sensing behavior. In addition, the effect of the micro/nanoscale structures on the strain induced resistance change was discussed to provide useful information for designing CNT-based polymer composites with high strain sensing capability.

Chapter 4 Electrical Resistance Change and Crack Behavior in Carbon Nanotube/Polymer Composites under Tensile Loading

This chapter studies the electrical and mechanical responses of cracked CNT-based polymer composites. Tensile tests were performed on single-edge cracked plate specimens of the nanocomposites at room temperature and liquid nitrogen temperature (77 K), and the electrical resistance change of the specimens was monitored. An analytical model based on the electrical conduction mechanism of CNT-based composites was also developed to predict the resistance change resulted from crack propagation. The crack induced resistance change was calculated, and a comparison of the analytical predictions against the experimental data was made to validate the applicability of the model. In addition, the fracture properties of the nanocomposites were assessed in terms of the J-integrals using an elastic-plastic finite element analysis.

Chapter 5 Loading Rate-dependent Fracture Properties and Electrical Resistance-based Crack Growth Monitoring of Carbon Nanotube/Polymer Composites under Tension

This chapter presents a combined numerical-experimental study on the loading rate-dependent fracture behavior of cracked CNT-based polymer composites under tension. Tensile tests at various loading rates were conducted on single-edge cracked plate specimens of CNT/polycarbonate composites. The electrical resistance change of the composite specimens was utilized to capture the crack behavior during the tests. An elastic-plastic finite element analysis was also employed to determine the fracture properties by means of the J-integral. In addition, scanning electron microscopy (SEM) observation was implemented to assess the fracture mechanisms of the CNT-based polymer composites under the different loading rates.

Chapter 6 Crack Growth Characteristics of Carbon Nanotube-based Polymer Composites Subjected to Cyclic Loading

This chapter presents the characterization of crack growth in CNT-based polymer composites under fatigue loading. Fatigue crack growth tests were performed on single-edge cracked plate specimens of CNT/polycarbonate composites at room temperature and 77 K. An elastic-plastic finite element analysis was also conducted to determine the J-integral range. The crack growth rate data were expressed in terms of the J-integral range, and the effect of nanotube addition on the fatigue crack growth behavior was examined. In addition, possible mechanisms of the crack growth in the nanocomposites are discussed based on microscopic observations of the specimen fracture surfaces.

Chapter 7 Conclusions

The main results and conclusions of the present research work are summarized.

論文審査結果の要旨

本論文は，次世代マルチファンクショナルデバイスの設計・開発および信頼性・安全性評価のためのカーボンナノチューブ（CNT）分散ポリマーコンポジットの電気抵抗・き裂挙動に関する理論的・実験的研究成果をまとめたもので，全編 7 章からなる。

第 1 章の序論では，本研究で取り上げた CNT 分散ポリマーコンポジットの力学的・物理的挙動や電気抵抗変化による変形・損傷検知機能に関する研究の位置付けを述べると共に，本研究の目的と意義を明らかにしている。

第 2 章では，多層 CNT 分散ポリカーボネートコンポジットの導電率測定を行い，導電率の CNT 体積含有率依存性を明らかにしている。また，CNT 分散ポリマーコンポジットの CNT 間トンネル効果を考慮した電気伝導に関する理論モデルを提案し，導電率に及ぼすマイクロ・ナノ構造の影響解明に成功している。続く，第 3 章では，多層 CNT 分散ポリカーボネートコンポジットの引張試験・電気抵抗測定を行い，ひずみと電気抵抗の関係を明らかにしている。また，CNT 分散ポリマーコンポジットの電気伝導に関する理論モデルを拡張し，ひずみの増大に伴う電気抵抗変化を求めて，ひずみ検知機能を考察している。これら理論解析・実験に基づく成果は，学術のみならず実用上の意義も大きい。

第 4 章～第 6 章では，引張負荷を受ける片側縁き裂を有する多層 CNT 分散ポリカーボネートコンポジットを取り上げ，電気抵抗・き裂挙動を理論・実験両面から解明している。先ず，第 4 章では，き裂を有する多層 CNT 分散ポリカーボネートコンポジットの静的引張試験・電気抵抗測定を室温・液体窒素温度（77 K）で行い，き裂進展量と電気抵抗の関係，荷重 - 変位曲線の非線形挙動を明らかにしている。また，き裂進展による CNT 電気伝導ネットワーク遮断メカニズムをモデル化し，電気抵抗変化を求めて，き裂検知機能を考察している。さらに，弾塑性有限要素解析により，実験結果に理論的検討を加え，破壊挙動の温度依存性を解明・考察している。第 5 章では，室温において顕著なき裂材の高速破壊に注目し，き裂を有する多層 CNT 分散ポリカーボネートコンポジットの高速引張試験・電気抵抗測定および弾塑性有限要素解析・電気抵抗モデル計算を行い，電気抵抗・き裂挙動の負荷速度依存性を解明・考察している。また，走査型電子顕微鏡（SEM）による破面観察を行い，破壊形態について検討を加えている。第 6 章では，室温・77 K における疲労き裂進展試験・弾塑性有限要素解析を行い，疲労き裂進展挙動の温度依存性を解明・考察している。また，SEM による破面観察を行い，破壊形態について検討を加えている。

最後に，第 7 章の結論では，各章で述べた内容を概括すると共に，得られた知見を整理し，本論文の統括としている。

以上要するに，本研究は，CNT 分散ポリマーコンポジットの電気抵抗・き裂挙動の理論的・実験的解明に成功し，高性能なナノコンポジットの設計・開発・評価に資する結果を提供したもので，材料システム工学の発展に寄与するところが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。